# EXTRAPOLATION OF EXPLOSIVE FORMULATIONS BASED ON WAX BINDER SYSTEMS TO HIGH PERFORMANCE

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**14. ABSTRACT**

Explosive formulations using wax binders with 83 to 86% RDX have demonstrated excellent resistance to bullets and fragments when loaded into heavy confinements. However, these lack the detonation pressure to replace Comp B in fragmenting warheads. This work examines use of waxes of high density to boost performance, yet keep fairly high wax content consistent with lower sensitivity. Theoretical calculations of performance detail what is possible, up to very high performance. Laboratory efforts to make small quantities of theoretically desirable formulations are described.

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# INTRODUCTION

Recent efforts to replace TNT in Army bursting charges had led to development of an RDX/plasticized wax formulation that can be melt cast into warheads. This material has undergone certain insensitive munitions (IM) testing in the M107 projectile. It displayed one especially interesting property, it had good resistance to bullet or fragment threats; it tested superior even to an insensitive plastic bonded explosive [PBX (of about same solids loading)] in this regard. Actually, this result is not so surprising, as this general property of wax binders was known more than 50 yrs ago (ref. 1). A formulation using 14% wax had passed the most violent bullet impact test being run at the time (circa. 1942). Also from reference 1, it was shown long ago that in nominally 60/40 cyclotols, the bullet impact resistance increases with the fraction of desensitizing wax added and there is significant change from the 1% in conventional Comp B to 3.8%. The motivation to further investigate wax binders is to keep this IM property and maintain the inherent cost advantages of a melt cast formulation while boosting the performance.

New RDXs being considered for use in United States munitions generally have better particle shapes than previously available. In particular, particles are more round, with smoother surfaces than was typical. The formulator has reported significantly lower viscosity, both in meltable binders and in cast cure mixtures, when using new particles as opposed to traditional particles (refs. 2 and 3). For example, reference 1 quotes that over 20% wax was necessary for satisfactory pouring. The new RDXs in class I and class V mixtures pour very well at 17% wax and have been cast even at 14%. In contrast, at 17%, the previous RDX using class I and V as before, makes a mixture too thick to cast (at least very well). These properties suggest to try to combine higher solids loadings of new RDX types with exploration of other waxes to attempt to make an explosive that has performance of Comp B, while retaining the bullet and fragment resistance characteristics of wax based formulations. We define "performance of Comp B" as a formulation with identical detonation pressure (so should have similar fragmentation ability) and equivalent cylinder energy (so should have same velocity on the fragments), at least out to seven volume expansions of the detonation products. Such a formulation would help in developing IMs, as bullet and fragment impact are an important threat to Army systems.

# ANALYSIS

Thermochemical code calculations (Cheetah code, ref. 4) were used to identify the performance potential possible from this approach. It was obvious that just trying to increase the solids load in the hydrocarbon wax binder system, as currently developed, has limits. Figures 1 and 2 show, theoretically, what is possible.
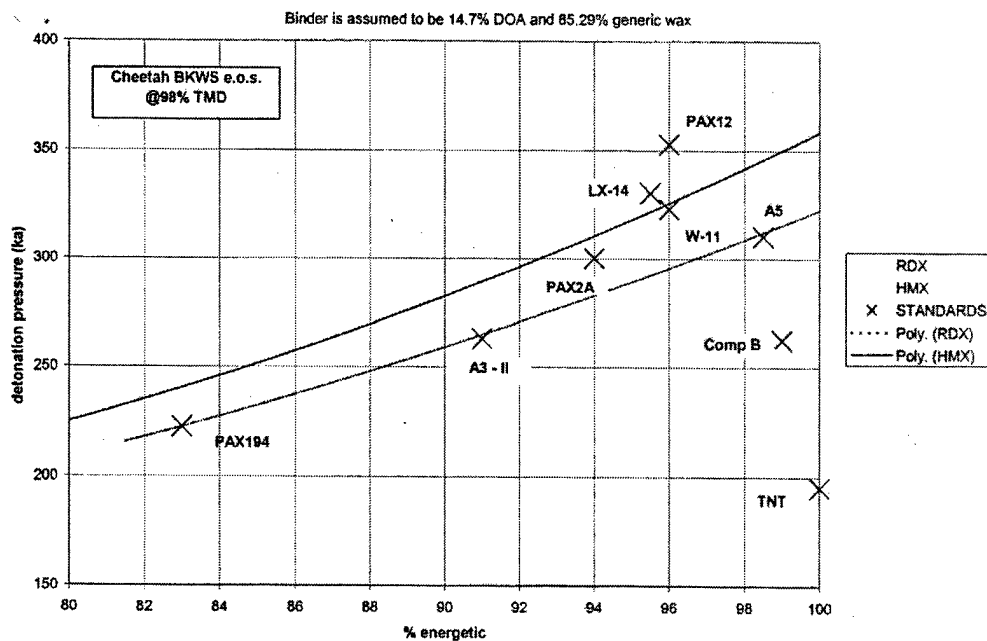
Binder is assumed to be 14.7% DOA and 85.29% generic wax



Figure 1
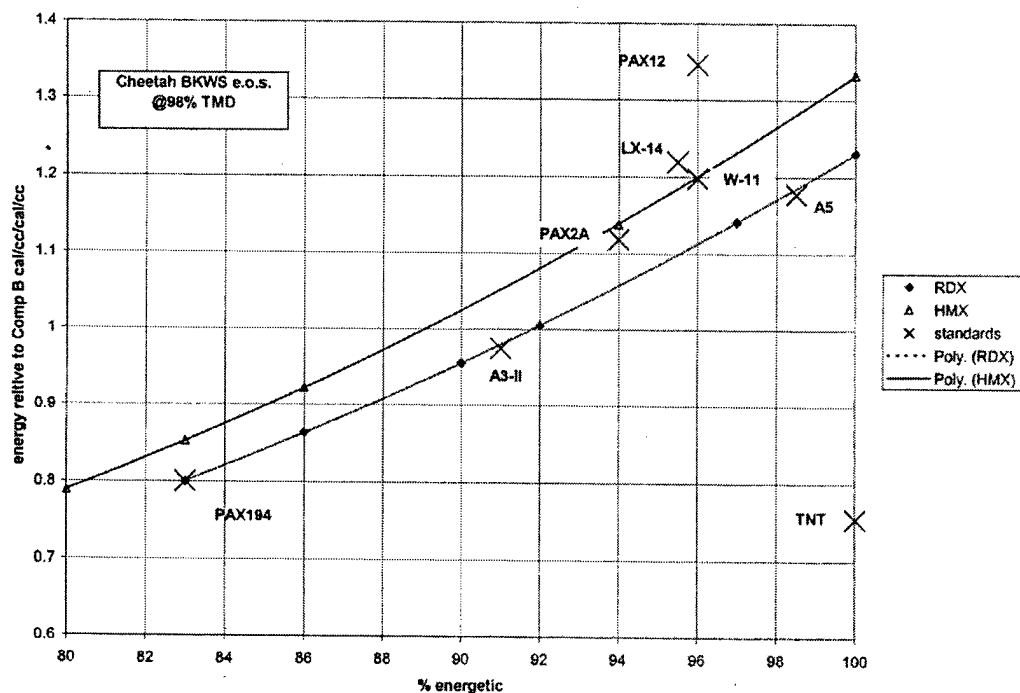Detonation pressure versus amount of energetic



Figure 2
Available energy output versus amount of energetic

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Figure 1 shows detonation pressure versus amount of energetic in the formulation. All calculations assume 98% theoretical maximum density (TMD). It is expected that the smaller the amount of energetic, the more insensitive the formulation, so generally, formulations at smaller percent would have better IM potential. Note: the total of all energetic materials in the formulation is plotted, so, for example, Comp B is plotted at 99% energetic constituents and PAX2A is plotted at 94%. The lower curve (dots) is based on adding more RDX to the wax, and the upper curve (solid) assumes HMX. To match Comp B in pressure requires about 91.5% RDX or 87% HMX. Figure 2 plots energy lost from the products by the time they expand to about three times their original volume versus amount of energetic. The energy scale is the work done by the expanding products per unit of original volume divided by the equivalent number for the Comp B reference. When this ratio is plotted versus volume, the relationship between different explosives tends to plateau by the time three volume expansions is reached; the curves are fairly flat as expansion continues. Thus, comparison is done at that volume where Comp B reaches approximately three volume expansions. In figure 2, materials are being compared at the same actual volume. Figure 2 shows about 92% RDX or 89% HMX is required to match Comp B, more-or-less in agreement with the pressure requirement.

Although not impossible, these are heavy solid loadings. Ninety-two percent RDX by weight in this formulation translates into 85.7% by volume; meaning 14.3% of the volume would be binder. An estimate for the empty volume between the RDX grains in a mixture of three parts class I to one part class V (about the best packing fraction) is 16.5%. So there would not be enough binder to float the particles apart. To approach 14.3% requires a trimodal RDX particle size distribution such as 6.75/2.23/1 of class 1/classV/4 μm that may be able to reach the low 14.3% value. Now that bulk quantities of 4 μm material have become available, it may be possible to make such a formulation. But, at best, it represents working at the limit.

There are other approaches to avoid the need for trimodal particle distributions. The typical approach to increase formulation performance is to pack more energy per volume into the formulation. This usually has the disadvantage of increasing the sensitivity of the formulation at the same time. On the one hand, if one just packs in more solids and presses to density, the previous available volume consideration show that many particles must be broken up or distorted in order to achieve the density. The pore space has to be filled in. On the other hand, if the binder is made energetic, then it may loose some of the ability to absorb externally applied energy without starting to react.

A different approach is to improve the charge density to get the desired detonation pressure and cylinder energy. The idea is to improve the efficiency of using the energy in the explosive formulation rather than increasing the total energy. Intuitively, this approach should lend itself towards less sensitive, high performance formulations, as a larger amount of inert binder can be maintained in the formulation. The concept is demonstrated using thermo-chemical calculations as follows. Figure 3 shows the same RDX formulation considered in figures 1 and 2 along with two hypothetical RDX formulations, where the wax used in the binder system is assumed to be more dense. The reason for picking these particular density values will become apparent later. Figure 4 shows the corresponding available energy plotted as before. The calculation was done using two different equations of state in Cheetah (BKWS and JCZS) to show the trends are similar although values do change.

There are grounds to select the Cheetah BKWS over the Cheetah JZCS calculations. It happens that one data point for pressure is available as indicated for the real wax binder system, but at slightly larger percent TMD than 98%. This point is from a witness plate dent, so should not be taken as an independent pressure measurement. Basically, the dent ranks an unknown pressure vis-à-vis dents from reference explosives. As seen in figure 3, the JCZS calculations would take the 83% RDX material to about the TNT pressure, implying its dent should be the same. However, the reported pressure value implies the dent must be about halfway between TNT and Comp B. Right where the BKWS calculations indicate it should be. A similar situation occurs when considering exp6 Cheetah calculations vis-à-vis BKWS. We conclude the BKWS is better at calculating pressure. It is demonstrably much better than the others at calculating the correct detonation velocity.
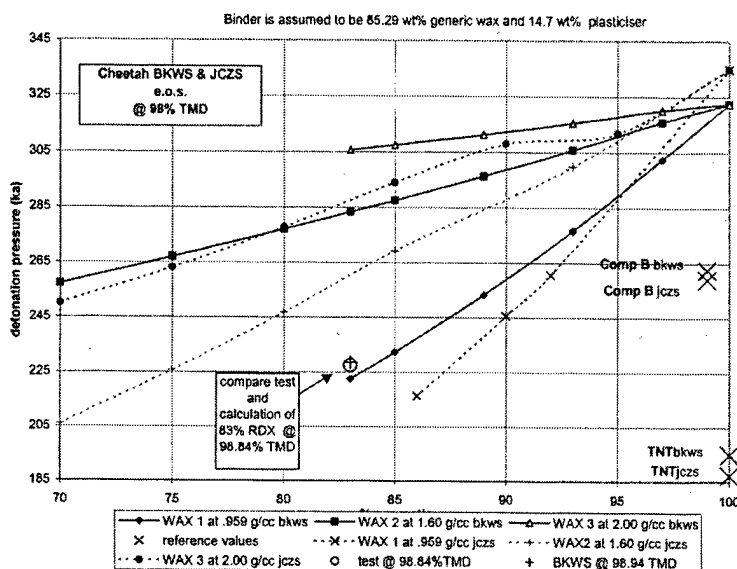


Figure 3
Effect of wax density on detonation pressure

The measure of explosive output in the laboratory is the cylinder test, from which Gurney energies are obtained. When the square of the ratio of measured Gurney energy to measured Comp B Gurney energy is plotted against the ratio of calculated energy output to Comp B calculated energy output, both at the respective volumes corresponding to the 19-mm expansion of the cylinder test, the BKWS calculation is about the same as exp6 or JCZS calculations in correlating test data. For all three equations of state, points representing LX-14, Comp A-3, PAX194, and TNT are close to the 45 deg line; indicating all calculations properly rank the cylinder test results. Yet again, BKWS is slightly superior, but differences are minor. Because BKWS Cheetah calculations seem to give good results, the BKWS equation of state will be used for the remainder of this paper.

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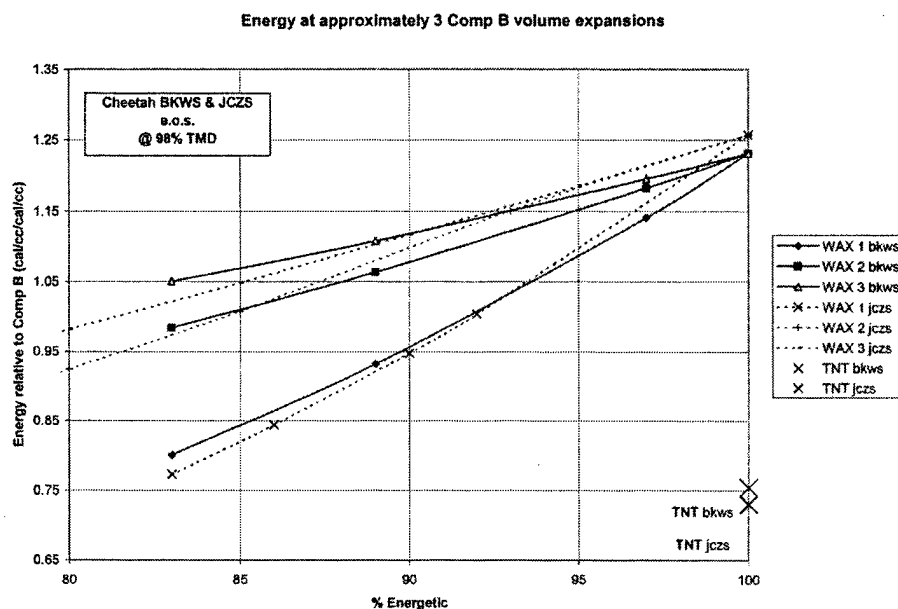**Energy at approximately 3 Comp B volume expansions**



Figure 4
Effect of wax density on available energy

It seems that remarkable improvements can be expected just from adjusting binder density. Adopting the BKWS calculations, with the 1.60 g/cm$^3$ "wax 2" only 74% RDX is required to obtain Comp B detonation pressure, although 84% is needed to give the required available energy. But, even 84% is a big relief from the situation of figures 1 and 2. At 84% by weight, RDX only constitutes 80.69% of the volume and the 19.32% volume occupied by binder can easily float a class I/class V mixture apart. The total specific energy from detonation in the two 84% formulations, one with wax at 0.953 g/cm$^3$ and the other with wax at 1.60 g/cm$^3$, is the same (1540.57 cal/g at the end of the release isentrope), but of course, it is different on a per volume basis. The detonation energy for wax 2 @ 84% (when the products have been returned to STP) at 1540.57 cal/g is almost the same as Comp B (1544.26 cal/g). But the blast energy is different. Energy at the end of the release isentrope for the wax 2 version is 1302.7 cal/g and for Comp B is 1377.87 cal/g, still a minor difference. A significant difference is that the wax 2 formulation has higher detonation pressure than Comp B.

The effect of density in improving detonation pressure seems obvious. There is more than 8% more moles of gas per unit volume created in the detonation with wax 2. The effect on expansion energy depends on where it is measured. Figure 5 shows the release isentropes.
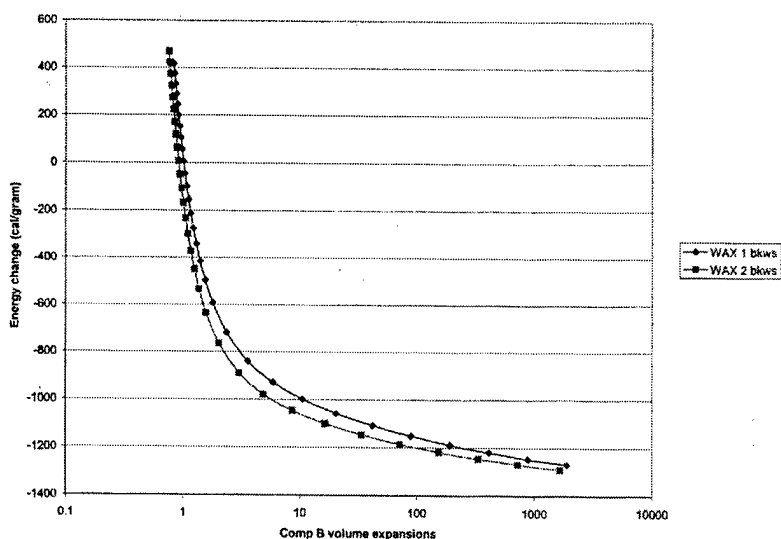
Figure 5
Release isentropes

There are large differences in energy yield at small volume expansions. Figure 6 plots the increase in energy per gram of 83% RDX/wax 2 over the 83% RDX/wax 1 based on figure 5. The difference in energy/gram is 13.4% at three volume expansions and still 8.6% at seven volume expansions (the usual cutoff expansion for determining fragment kinetic energy). That is, over the useful range, about 10% more energy per gram (or ~22% more per initial cubic centimeter) is outputted by the wax 2 system over the wax 1 system. This advantage goes away as the products expand out to atmospheric pressure. When P=1 atmosphere, the difference in energy per gram has reduced to only 1.6%. Which means it is a small advantage to raise the wax density if the only intent is to produce blast without fragments. The advantage comes in producing and launching fragments.
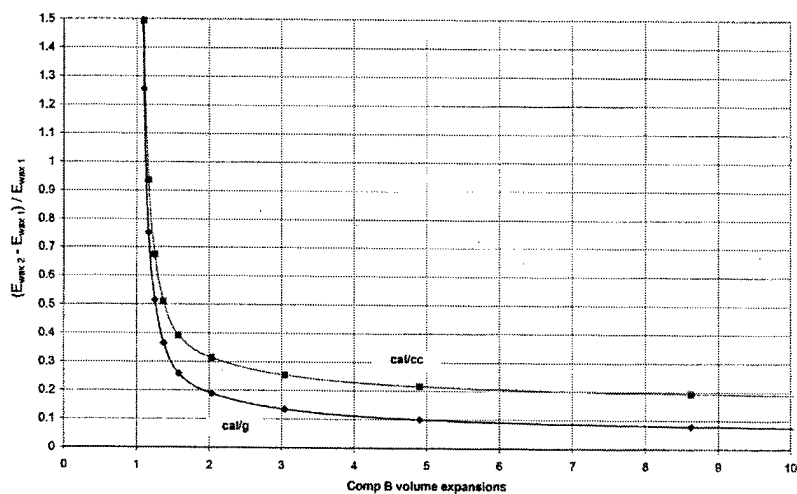


Figure 6
Energy difference on the two release isentropes

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These results provide motivation to search for more dense wax binders. It happens that certain commercial waxes, namely the chlorowaxes and the fluorowaxes have the densities assumed in figures 3 and 4. These may still contain some hydrogen, but they increase density by adding either chlorine or fluorine to replace some or all hydrogen. Materials considered in this work could be represented chemically as chlorowax, $C_{14}H_{29}Cl_{21}$ and fluorowax, $C_2F_3Cl$. Having halogens in the binder will cause some changes in the reaction chemistry. Most notably, by increasing the products average molecular weight. There will also be a slight increase in energy.

## CHLOROWAX AND FLUOROWAX

Chlorowaxes and fluorowaxes were considered in conjunction with RDX since the 1950's. But, the motivations were different. In reference 5, both a chlorowax and a fluorowax were investigated to make a version of Comp A3. The waxes chosen had low molecular weights and thus low melting points. In fact, the chlorowax was rejected because it melted at too low of a temperature. The fluorowax formulation was, to a considerable extent, pressable, but wasn't as easy to use as usual Comp A3 in a high-speed production application. There was not effort to measure performance differences caused by the chlorowax, as only production issues were investigated. More recently, Machacek et al. (ref. 6) investigated chlorowax mixed with Comp B. Included in this reference is work done at the Armaments Research, Development and Engineering Center (ARDEC), Picatinny, New Jersey on the closed bomb-burning rate of these formulations. They chose four chlorowaxes, three were room temperature oils and one was solid. Only the solid had the high density of 1.6 g/cm$^3$. The oils were lower, down to 1.4 g/cm$^3$. Their wax selection was based on the desire for all to be liquid below the melting temperature of TNT. They found all candidates were completely miscible in molten TNT.

When they tested their charges using the underwater shock and bubble energy test, they generally found the shock energy inferior to Comp B (expect for one formulation at 5% chloro-wax), while the bubble energy was less affected. These measurements can be compared with results from our calculations to gauge how well we can predict. The 1.6 g/cm$^3$ solid seems to be equivalent to the chlorowax that will be considered, so it will be assumed to have the same properties for calculation. Assume the underwater shock energy relates to the energy released by the time the explosion products have returned to atmospheric pressure. Figure 7 plots the measured values divided by the respective measured value for Comp B against the calculated energy divided by the respective calculated energy for Comp B. The 5% and 10% points for shock energy are satisfactorily close to the 45-deg line, but the 20% point has more shock energy than calculation predicts. Bubble energy, which includes lots of late time effects, doesn't correlate much at all. Basically, about the same plot is obtained whether the x-axis is total release energy, release at ~7 $V_o$ expansion or the heat of detonation (products return to STP) and is not materially changed if the Cheetah JCZS equation of state is substituted. It seems that Cheetah calculations under predict the bubble energy at high chlorowax percentages.

Another feature was that for all candidates, adding 5% chlorowax increased the charge density from neat Comp B, even for the low-density oils. Adding more than 5% of the three lower density candidates predictably decreased the density, while the candidate with 1.6 g/cm$^3$ only drops back to the neat Comp B value beyond 5%. This must mean that at least the light weight oils are filling voids present in the neat Comp B at the 5% level, and don't decrease

density until these voids are full. There were significant increases in card gap initiation pressure with some of the candidates, with the lowest density oil dropping sensitivity to almost TNT level with only 5% addition, also indicative of voids being filled. All formulations with added chlorowax were less sensitive then Comp B, but there is a huge variation in the effect between candidates and with what fraction of chlorowax was added. Sometimes sensitivity decrease with increasing wax and sometimes it increased.
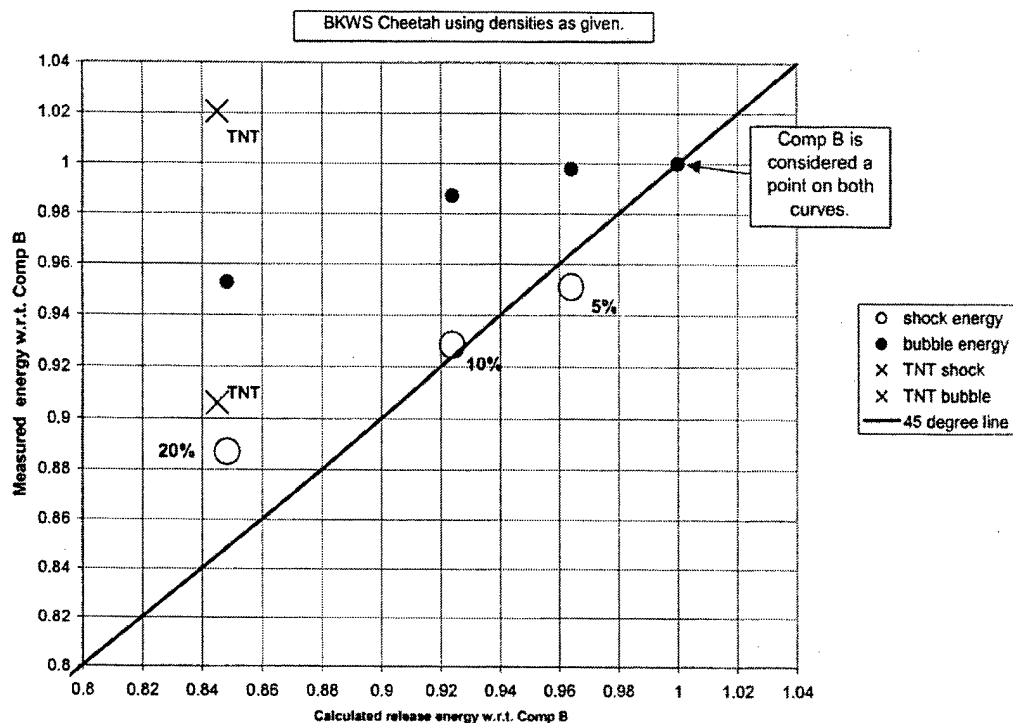


Figure 7
Compare calculated energy with underwater energy measurement

The closed bomb work described in this report showed these waxes always slow the Comp B burning rate, with the effect up to a factor of half. More wax gives more slowing. But, when the wax was precoated on the RDX before making the formulation, only 1% wax cut the burning rate by half and was as effective as mixing in 20% during processing. It was thought that both a physical cocoon of protective wax around RDX particles and the halogen flame suppression property are acting to slow burning, and precoating invokes both processes to the maximum. It was not explained why the molten TNT doesn't displace chlorowax from the RDX surface given the wax is fully soluble in TNT. In summary, there was evidence that chlorowax might interfere with slow (burning) reactions in Comp B without really identifying whether the effect is physical or chemical.

Consider solid chlorowax as a binder for RDX. Calculations assuming generic chlorowax binder are shown in figures 8 and 9.

Figure 8 indicates Comp B pressure requires about 75% RDX or 71% HMX. Figure 9 gives 80% and 75%, respectively, to match available energy. The detonation energy of the chlorowax formulation (1377.04 cal/g) is smaller than that of the "beefed up" $\rho=1.6$ g/cm$^3$ wax 2

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with 84% RDX (1540.57 cal/g), but, similar to the energy at the end of the release isentrope (chlorowax = 1265.95 cal/g and beefy wax = 1302.70 cal/g using Cheetah with BKWS). Thus, the extra detonation energy in the beefy wax is not usable. According to Cheetah, beefy wax delivers its energy almost the same as the chlorowax at early expansions, so at three Comp B volume expansions it has delivered 910.49 cal/g to fragments, while the chlorowax has given up 89.43 cal/g.
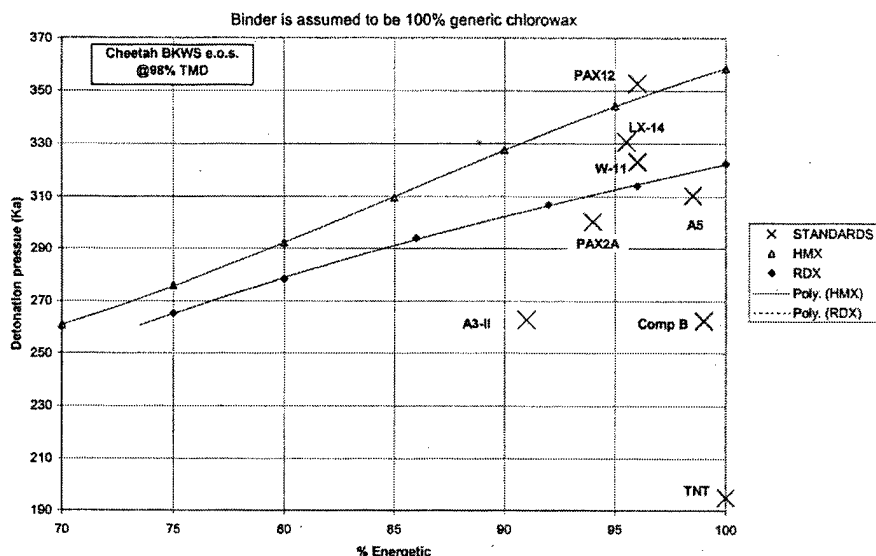


Figure 8
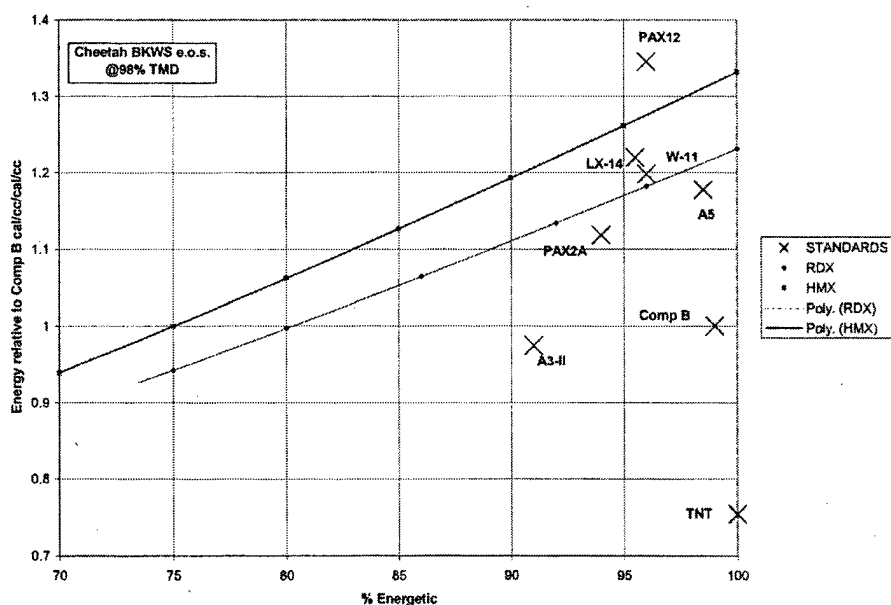Detonation pressure versus amount of energetic



Figure 9
Energy output versus amount of energetic

When fluorowax is substituted as a binder, figure 10 indicates 72% RDX can match detonation pressure while figure 11 shows energy will exceed Comp B. With fluorowax, the limiting factor becomes reaching the detonation pressure in contrast to chlorowax and "beefy" wax, where energy is the determining parameter.
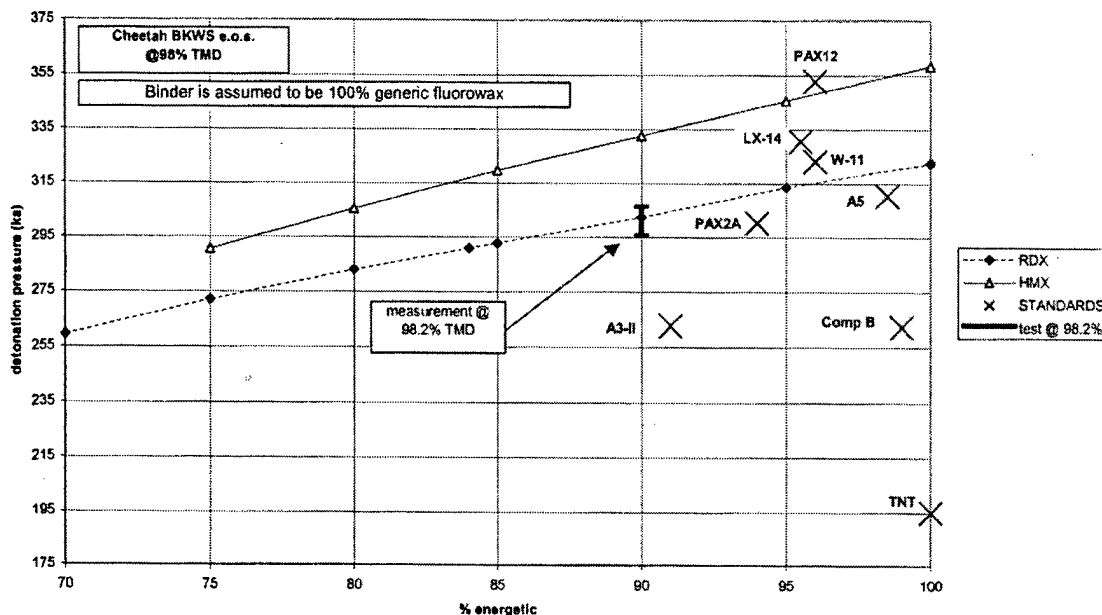


Figure 10
Detonation pressure versus amount of energetic

As shown, levels of solids loading to match Comp B are much less demanding with chlorowax and fluorowaxes than with normal hydrowax. For example, when considered as volume fraction, the 80% RDX mixture actually has 22.1% chlorowax by volume, more than enough to float the particles in a bimodal mixture of class I and class V apart. Even better, the 72% RDX in fluorowax has 26.1% by volume for the wax.

Figure 10 also shows a further interesting property of the chlorowax and fluorowax formulations. They can be extrapolated to very high detonation pressures with HMX, above that of LX-14. In fact, predictions are closer to the experimental high performance PAX12 than to LX-14. It is unlikely that formulations at such high solid loadings can be very insensitive. According to figures 10 and 11, a LX-14 equivalent would have roughly 10 ~ 11-wt% inert binder. At 89-wt% HMX, the formulation would have only 11.5% binder by volume (HMX and fluorowax are similar in density, so not much difference between weight % and volume %). Since a packing factor of 88.5% for HMX particles would be difficult, press loading along with its attendant deformation and crushing of HMX would be needed to make a charge. A situation not suited to low sensitivity. The LX-14 has a special multimodal particle size distribution to attempt to alleviate this problem, but turns out to be especially poor in IM characteristics. The 89% formulation has twice as much binder at LX-14, which should help. Having more binder always makes it easier to reduce deformation and crushing. Thus, there seems potential to have LX-14 performance with improved (not necessarily IM) sensitivity properties.
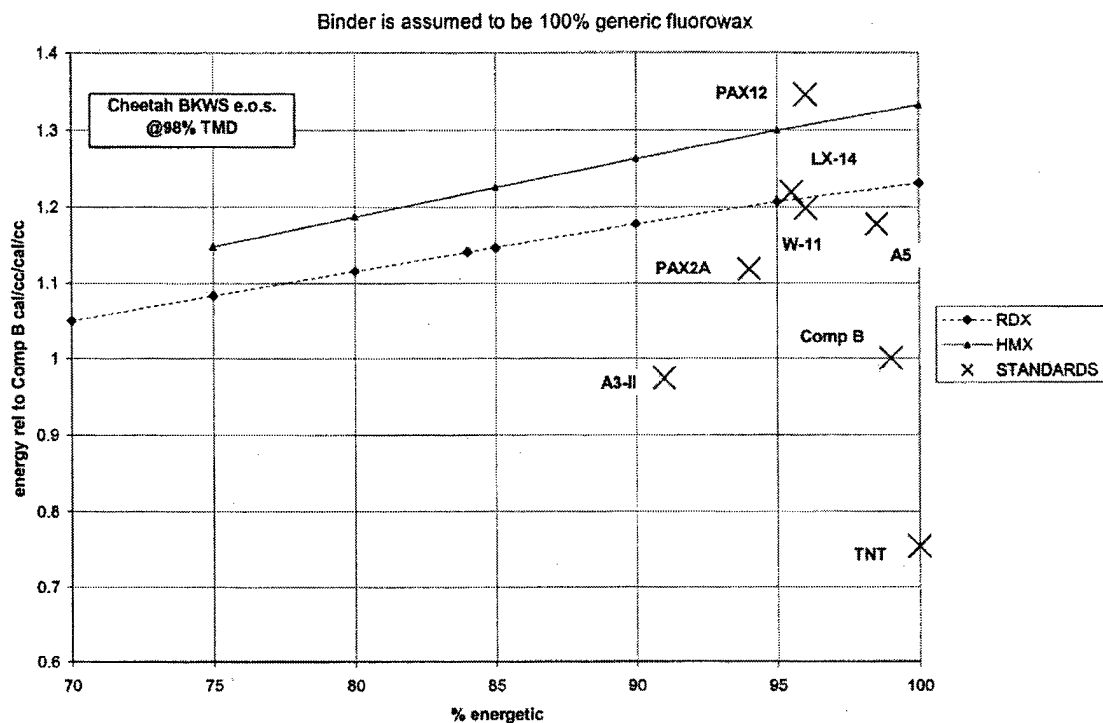
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Figure 11
Energy output versus amount of energetic

It also seems possible to have a PAX2A look alike using 91% RDX with chlorowax or 89% RDX with fluorowax. As before, the solids loading is determined by the need to match energy in the case of chlorowax and the need to match pressure with fluorowax.

Pressed pellets of 90% RDX and 10% fluorowax were fabricated and detonation velocity and witness plate dent measured. The material pressed quite satisfactorily. Detonation velocity is compared with predictions in the table. Again, the BKWS equation of state gives a good prediction.

Table 1
Detonation velocity results

| Source | Velocity (km/s) |
|--------|-----------------|
| Experiment | 8.44 at 1.7997 g/cm$^3$ (1.8% voids) |
| BKWS Cheetah | 8.45 at experimental density |
| JCZS Cheetah | 8.18 at experimental density |
| EXP6 Cheetah | 8.58 at experimental density |

Test results were essentially the same in two other shots, showing very good repeatability. For example, the three dents were 0.158 in., 0.160 in., and 0.159 in. Dents from reference explosives TNT, Comp A-5, PBX9501, and TNAZ were plotted versus calculated detonation pressure. Then, the linear regression of these points was taken as the relationship of

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detonation pressure to dent. The shot with detonation velocity 8.44 km/s shown in the table gave 0.160 in., which translates into between 295.9 ~ 306.4 kilo-atmospheres according to the dent calibration. This result is indicated on figure 10 and, as before, the dent data seems consistent with Cheetah BKWS calculations. Detonation pressure seems about the same as for PAX2A explosive, but slightly less than Comp A-5 at 98% TMD. The Comp A-5 used in the dent calibrations was only at 94 ~ 95% TMD, and produced dents smaller than the fluorowax material. Of particular interest is that, as predicted, pressure is above that of Comp A-3, type II even though the A-3 has 1% more RDX.

Theoretically, chlorowax and fluorowax as binders seem attractive to take the wax binder approach up to high performance levels. The practicality of this approach depends on the properties available from these wax types, such as melting temperature; melt viscosity, wetting capability, and strength at operational temperatures. These will determine if, say, the 80% RDX with chlorowax can be poured or not. Work was undertaken to determine if such a formulation could be made and assess its properties.

## FORMULATION EFFORTS

Two types of chlorowaxes and three fluorowaxes were investigated, along with two chloro-oils and some common plasticizers. Chlorowaxes were supplied by Dover Chemical Corp. The selected products were Chlorez 700S (melts at 90 to 93°C) and Chlorez 700SNP (melts at 93 to 98°C). Both have a density of 1.6 g/cm$^3$. The chloro-oils were Paroil 170T and Paroil 170LV. Both have density just slightly less than 1.5 g/cm$^3$. The oils have lower average molecular weight than the waxes, and are liquids at room temperature. None of these materials are toxic. The Chlorez 700SNP formed large crystals at room temperature after a sufficient time, even when mixed with Paroil 170LV. Chlorez 700S stays "gummy" at room temperature. The oils, of similar chemical structure to the chlorowaxes, were used to modify the melting temperature of these waxes. Melting is not as sharply defined as for hydrocarbon waxes. They soften over a temperature range and this range can be adjusted by plasticizing with the oils. Mixtures of waxes with the oil have no vapor pressure and did not separate during repeated melting and cooling. The chlorowaxes are compatible with RDX. Because the oil continuously drops the melting temperature with increased amounts, there is a limit on how much can be used to plasticize the wax before the melting temperature drops too low. It turns out that not enough oil can be used to reduce viscosity sufficiently for successfully blending in the solids. About 35 wt% Paroil 170LV reaches limits on the melting temperature. A formulation of 62.25% class 1 RDX, 20.75% class V RDX (i.e., 3:1), 11.05% Chlorez 700SNP, 5.36% Paroil, and 0.60% Citroflex A-4 was tried, but would not mix well in a 500 g batch even when using the new, very high quality, rounded RDX particles. These were the same particles known to thin hydrocarbon wax formulations noticeably. It was too thick to pour.

The usual formulation plasticizers, DOA and IDP don't work with chlorowaxes. But, citric acid ester based plasticizers; Citroflex A-2 and A-4 worked and A-4 gave good thinning of the melt. It also caused the softening point to the chlorowax to drop, like the Paroil, and could not exceed 25% for this reason. A mixture of 15% Citroflex A-4 with chlorowax was selected to formulate with RDX. Although viscosity was not measured, this binder itself, displayed a very fluid behavior at 90 ~ 100°C, but, gelled before the desired RDX amount (80%) could be mixed in at 102°C. It was found difficult to pour at 60% RDX and completely gelled at 70%.

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This is too low to meet Comp B performance. It is significantly lower than the 83% plus solids loading already demonstrated using hydrowaxes. This melted chlorowax binder seems inherently too thick to formulate at required solids loading of 80%.

Halowax 600 (melts between 59 and 62°C), Halowax 1500 (melts between 79 and 87°C) and Halowax 2300 (melts between 97 and 105°C) were the three fluorowaxes investigated. All came from Halocarbon Products Corporation. Numbers refer to average molecular weight of the material. These materials have density of 2.0 g/cm$^3$. Basically, these materials are blends of solids and oils, with the oil used as plasticizing agent. Thus, the Halocarbon 600 has more oil than 1500, etc. As average molecular weight goes up, the materials become stiffer. However, all have a gummy feel at room temperature and are relatively tacky. None of these had visible crystallization. All are compatible with RDX. Upon heating, these materials softened without a defined melting point. Viscosity of the melt was excessive. They do not appear suitable for a melt cast application.

## COMBINING APPROACHES TO OBTAIN REDUCED SENSITIVITY

After finding that a melt pour formulation could not be obtained, other approaches that could lead to Comp B or better performed and reduced sensitivity were investigated. It was found easy to coat RDX with fluorowax to make a powder suitable for other processing techniques. Data on pressed pellets is included in figure 10. Also, the coated material is available for use in cyclotols (like the chlorowax coated RDX mentioned in reference 6) or cyclotol like formulations that have other (less sensitive) materials substituting for TNT. Theoretically, it is possible to significantly increase the level of desensitizing wax in such formulations from the usual 1% and still match Comp B. Halowax 2300 has a high melting temperature, guaranteeing it will stay on the RDX particles during the casting process, a potential problem wit the chlorowax used in reference 6. Summarizing, this is the energetic binder approach, but with the binder system better layered to physically separate the two explosive elements.

## CONCLUSIONS

Theoretically, a formulation of RDX with wax binder made from chlorowax or fluorowax is very attractive. But, our efforts failed to find a melt castable, insensitive munitions (IM) explosive formulation using this idea when we used only class I and class V RDX stocks. The properties of the melted waxes led to mixtures too thick to pour at suitable temperature, even when using the new, high quality RDX materials. But, the benefits indicated by theory are strong enough to motivate exploring other means (e.g., other particle distributions or precoating of RDX) to reduce formulation viscosity enough to allow pouring. Further studies are scheduled.

# REFERENCES

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